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## USE OF A MAGNESIA-ZIRCONIA BRICK

### DESCRIPTION

Fireproof materials and products may be divided roughly into basic and non-basic products.

The group of basic (fired) products includes magnesia-zirconia products (referred to in the following as MZA) and products based on magnesia-zircon (referred to in the following as MZ).

MZA products are typically manufactured on the basis of sintered and/or fused magnesia and zirconium dioxide ( $\text{ZrO}_2$ ). Mineralogically, they include periclase ( $\text{MgO}$ ) and stabilized or non-stabilized zirconium dioxide, and they frequently contain, sometimes in small amounts, calcium zirconate, as well as small quantities of silicate phases.

If the zirconium dioxide is partially or completely stabilized, a direct bond  $\text{MgO-ZrO}_2$  is produced through diffusion procedures. The mechanical heat properties are improved in this way.

MZA bricks have a high spalling resistance and a high refractability. They are therefore used above all in rotary tubular kilns or shaft kilns in which lime, dolomite, magnesite, or cement are calcined.

A typical batch for MZ products contains sintered and/or fused magnesia and zirconium silicate ( $\text{ZrO}_2 \times \text{SiO}_2$ ). The zirconium silicate reacts with the  $\text{MgO}$  to form forsterite and stabilized zirconium dioxide. Typically not the entire  $\text{MgO}$  component is converted into forsterite. Therefore, mineralogical periclase components remain in the brick. Because of their good chemical resistance, above all to alkalis, alkalis salts, and/or  $\text{SO}_2/\text{SO}_3$ , MZ products are used in regenerator chambers of glass melting furnaces.

This related art and exemplary formulas of MZA/MZ products may be found in the "Taschenbuch feuerfeste Werkstoffe [Handbook of Fireproof Materials]" by Gerald Routschka: (ISBN 3-8027-3146-8).

The present invention is directed to the magnesia-zirconia products known per se, but uses them in a regenerator chamber of a glass melting furnace which is operated at least temporarily or periodically with a reducing atmosphere.

As noted in the introduction and cited in Routschka, until now magnesia-zircon products have been used in the packing of glass melting troughs, particularly in the alkali sulfate condensation region of such a packing. The temperature in this region is from 800 to 1100°C.

In order to reduce the  $\text{NO}_x$  content in the exhaust gas, it has been suggested that a glass melting trough be operated with a reducing atmosphere. The  $\text{NO}_x$  content in the exhaust gas may be reduced by factor of 3 to 6 in this case.

It is disadvantageous that reducing "skeins" arise in the regenerator chambers on the exhaust side, which negatively influence the service life of the magnesia-zircon bricks. At least partial decomposition of the forsterite ( $\text{Mg}_2\text{SiO}_4$ ) in the material into sodium/magnesium silicates occurs. The  $\text{CaO}$ -containing silicate phases are also converted. As a result, the packing no longer has the required stability.

Surprisingly, it has now been determined that problems of this type may be avoided if, instead of the known MZ products recommended for regenerator chambers of glass troughs, those based on magnesia-zirconia (MZA) are used.

The decisive advantage is suspected to be that these products have a significantly lower proportion of silicates than the MZ products, so that the destruction of the microstructure described above does not occur or occurs to a significantly reduced extent.

ZrO<sub>2</sub> is extremely corrosion-resistant to the corrosive materials in the condensation region of the alkalis, even if the glass melting tank is operated with a reducing atmosphere and a reducing atmosphere accordingly reaches the regenerator chambers. This is also analogously true if the glass melting tank is only temporarily operated with a reducing atmosphere.

For the use claimed, the thermal conductivity (WLF) of the bricks (packing bricks) is an important parameter, as is the specific heat capacity (C) or volume-related heat capacity (product of specific heat capacity C and apparent density R). In addition, the ratio of thermal conductivity to the specific or volume-related heat capacity is of interest.

Good values are achieved for all parameters using the MZA products cited, i.e.:

- the high thermal conductivity ensures the desired rapid passage of the heat through the brick,
- a specific heat capacity which is approximately 50% higher than zirconia bricks, for example, allows more heat to be stored,
- a favorite/more rapid temperature equalization is made possible through a higher value of the thermal diffusivity (over 1 m<sup>2</sup>/sec.).

MZA products also have significant advantages in relation to  $C_2S$ -bonded magnesia bricks. The periclase and the  $CaO$  in the dicalcium silicate phase of the  $D_2S$  products are converted by  $SO_3$  in the exhaust gas into sulfates or sulfides, respectively. This again results in destruction of the brick microstructure.

The lower the  $SiO_2$  content (the silicate phase), the more favorable the properties of the brick are for the application cited. The  $SiO_2$  content is thus to be less than 1.0 weight-percent, and according to another embodiment it is to be less than 0.5 weight-percent (in relation to the total batch and/or the total molded part).

The  $CaO$  content ( $CaO$  able to be provided as calcium zirconate, for example) is below 2 weight-percent according to one embodiment.

The mineralogical composition of the MZA product may move within the known ranges (Routschka, op. cit.).

The product comprises 5 to 35 weight-percent  $ZrO_2$ , 65 to 95 weight-percent  $MgO$ , and at most 5 weight-percent other components.

According to one embodiment, the product contains at most 2% other components.

The open porosity, determined in accordance with DIN EN 993-Part 1, is to be between 11 and 15 volume-percent, or between 12 and 14 volume-percent according to one embodiment.

After firing above  $1700^\circ C$ , an apparent density between 3.20 and  $3.55 \text{ g/cm}^3$ , or between 3.25 and  $3.40 \text{ g/cm}^3$  according to one embodiment, may be achieved. In this case, the apparent density is determined in accordance with DIN EN 993-Part 1.

The cold compression strength, determined in accordance with DIN EN 993-Part 5 on the fired product, is between 50 and 150 N/mm<sup>2</sup>, or between 70 and 85 N/mm<sup>2</sup> according to one embodiment.

The thermal conductivity (determined according to "class", among other things, in Ber. Dtsch. Keram. Ges. [Report of the German Ceramics Society] 34 (1957), 183-189) is in the range of 3-4 W/Km (at 1000°C).

The material grain sizes of the batch are not subject to any restrictions in principle. The proportion of zirconium dioxide, which may be introduced through baddeleyite, as commercially produced zirconium dioxide (unstabilized, partially stabilized, or completely stabilized), is in the grain range < 0.5 mm, for example, divided (approximately) in half between < 0.1 mm and 0.1-0.5 mm, according to one embodiment.

The component of sintered magnesia or fused magnesia is used in the grain range up to 6 mm according to one embodiment. In this case, the component > 1 mm may make up half to two-thirds of the total magnesia charge. In the following, two formulas/batches are specified, including the property features achieved after firing.

The bricks thus manufactured were successfully tested in an engineering experiment which stimulated the conditions occurring in operation of a packing (of a glass melting trough). The bricks were particularly tested under reducing atmosphere and showed themselves to be superior to conventional magnesia-zircon bricks.

	Sample 1	Sample 2
Magnesia (MgO) <1 mm	30%	20%
Magnesia (MgO) 1-6 mm	50%	50%
ZrO <sub>2</sub> 0.1 to 0.5 mm	0	15
ZrO <sub>2</sub> < 0.1 mm	20	15
Green apparent density (g/cm <sup>3</sup> )	3.32	3.46
Firing (°C)	1750	1750
Apparent density after firing (g/cm <sup>3</sup> )	3.35	3.50
Open porosity (%)	12.5	14
Cold compression strength (N/mm <sup>2</sup> )	55	80